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Lithiated amidines: syntheses and structural characterisations

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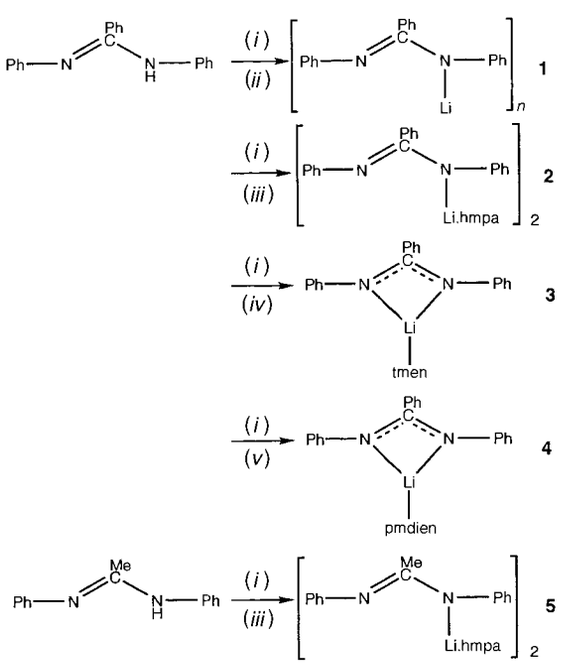
The reaction of a toluene solution of PhNC(Ph)NHPh (*N*,*N*′-diphenylbenzamidine) with *n*-butyllithium gave the toluene-solvated amidinolithium compound $\{Li[PhNC(Ph)NPh]\}_n$ **1**. Similarly the same reaction performed in the presence of the Lewis-base donors $(Me_2N)_3PO$ (hmpa), $Me_2N(CH_2)_2NMe_2$ (tmen) or $[Me_2N(CH_2)_2]_2NMe$ (pmdien) yielded the amidinolithium complexes $\{Li[PhNC(Ph)NPh\cdot hmpa]\}_2$ **2**, {Li[PhNC(Ph)NPh]·tmen} **3** and {Li[PhNC(Ph)NPh]·pmdien} **4** respectively. In addition the reaction of a toluene solution of the related amidine PhNC(Me)NHPh (*N*,*N*′-diphenylacetamidine) with $LiBu^n$ in the presence of hmpa afforded $\{Li[PhNC(Me)NPh\cdot hmpa\}_2$ **5**. The solid-state structures of **2**–**5**, which have been resolved by single-crystal X-ray diffraction methods, show both similarities and differences. The complexes **3** and **4**, which contain the di- and tridentate ligands tmen and pmdien respectively, are monomeric, whilst use of the unidentate Lewis base hmpa results in dimers **2** and **5**. However, the way in which dimerisation is achieved differs. The co-ordination geometry about the lithium cation is clearly influenced by the choice of donor and as such shows how a change in the denticity of the donor ligand utilised can have a significant effect on the solid-state structure of the system.

The use of homogeneous catalysis in the chemical industry has expanded continuously, largely due to and assisted by the rapid growth in studies of the metal–alkene, –allyl and –alkyne complexes which are important in catalytic processes.[1] The principles established for hydrocarbon reaction systems apply equally to heteroatom-containing systems, though the chemistry of the heteroatom, especially with respect to its co-ordinating ability, must be taken into account. As a result there has been increasing interest in pursuing the study of important pseudo-allyls, such as amidines [RNC(R′)N(H)R″; R, R′, R″ = *e.g.* permutations of H, Ph, Me, *p*-tolyl], with respect to their transition-metal co-ordination chemistry. Recently, this work on amidine co-ordination compounds has been reviewed comprehensively by Barker and Kilner.[2]

Several methods have been used to synthesize amidino-transition-metal complexes, but prominent among these has been the *in situ* reaction of an amidinolithium with a metal halide.[2] However, despite this extensive use as synthetic precursors, lithiated amidine compounds themselves have not been well documented. Indeed published work on them is restricted to a short metallation study *via* infrared spectroscopy,[3] the crystal structures of a series of arylbis(trimethylsilyl)amidinate complexes $\{Li[MeC_6H_4C(NSiMe_3)_2]\cdot thf\}_2$ (thf = tetrahydrofuran),[4a] $\{Li[4\text{-}XC_6H_4C(NSiMe_3)_2]\cdot NCC_6H_4X\text{-}4\}_2$ (X = H or Me)[4b] and $\{Li[PhC(NSiMe_3)_2]\}_3\cdot NCPh$,[4c] and our preliminary communication of the synthesis and crystal structure of $Li[CPh(NPh)_2]\cdot pmdien$[5] (pmdien = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine).

Here we report the syntheses and characterisations of five lithiated amidines (specifically, derivatives of *N*,*N*′-diphenylbenzamidine and *N*,*N*′-diphenylacetamidine) with and without complexation by the Lewis-base donors hmpa $O{=}P(NMe_2)_3$, tmen $[Me_2N(CH_2)_2NMe_2]$ or pmdien $[MeN(CH_2CH_2NMe_2)_2]$



Scheme 1 Synthesis of amidinolithium species **1**–**5**. (*i*) $LiBu^n$; (*ii*) toluene; (*iii*) toluene–hmpa; (*iv*) toluene–tmen; (*v*) toluene–pmdien

(Scheme 1). The four complexes, **2**–**5**, have been structurally characterised.

Results and Discussion

Compound **1** was prepared by lithiating a solution of *N*,*N*′-diphenylbenzamidine in dry toluene. Yellow microcrystals were

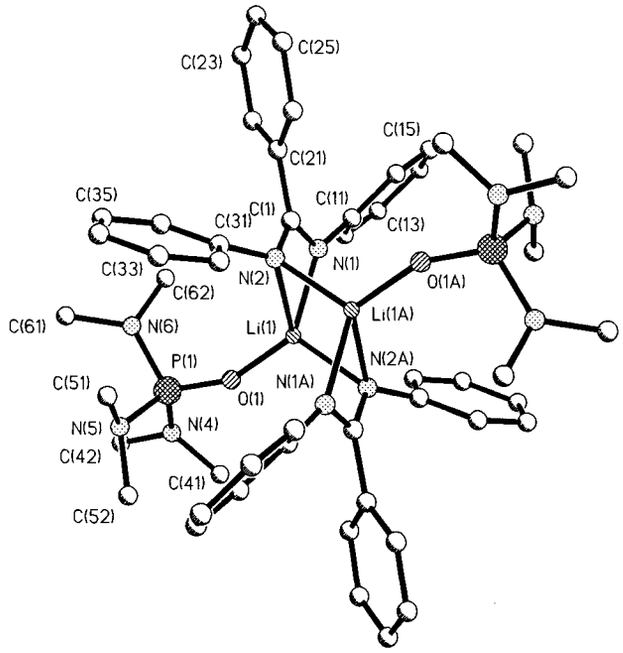


Fig. 1 Molecular structure of {Li[PhNC(Ph)NPh]·hmpa}$_2$ **2**. Hydrogen atoms are omitted for clarity in Figs. 1–4

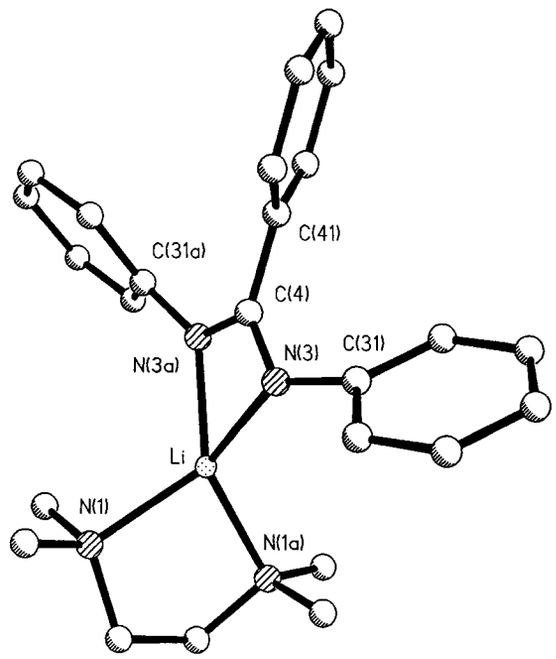


Fig. 2 Molecular structure of Li[PhNC(Ph)NPh]·tmen **3**

Table 1 Selected bond lengths (Å) and angles (°) for complex **2**

Li(1)–O(1)	1.834(6)	Li(1)–N(1)	2.046(7)
Li(1)–N(2)	2.173(7)	Li(1)–N(2A)	2.054(7)
O(1)–P(1)	1.476(3)	N(1)–C(1)	1.315(4)
N(2)–C(1)	1.349(5)		
O(1)–Li(1)–N(1)	122.5(3)	O(1)–Li(1)–N(2A)	117.8(3)
N(1)–Li(1)–N(2A)	112.8(3)	O(1)–Li(1)–N(2)	122.1(3)
N(1)–Li(1)–N(2)	64.9(2)	N(2)–Li(1)–N(2A)	104.9(3)
Li(1)–N(2)–Li(1A)	75.1(3)	P(1)–O(1)–Li(1)	154.5(3)
C(1)–N(1)–Li(1)	91.2(3)	C(1)–N(2)–Li(1A)	114.9(3)
C(1)–N(2)–Li(1)	85.0(3)		

Symmetry transformation used to generate equivalent atoms: A $-x + 1, -y + 2, z + 2$.

Table 2 Selected bond lengths (Å) and angles (°) for complex **3**

Li–N(3a)	2.023(4)	Li–N(3)	2.023(4)
Li–N(1a)	2.063(4)	Li–N(1)	2.063(4)
N(3)–C(4)	1.334(2)	N(3)–C(31)	1.395(2)
C(4)–N(3a)	1.334(2)		
N(3a)–Li–N(3)	67.6(2)	N(3a)–Li–N(1a)	134.83(8)
N(3)–Li–N(1a)	119.56(8)	N(1a)–Li–N(1)	87.7(2)
C(4)–N(3)–Li	88.69(14)		

Symmetry transformation used to generate equivalent atoms: a $-x, y, -z + \frac{1}{2}$.

isolated after 12 h at room temperature and shown by spectroscopic techniques to be {Li[PhNC(Ph)NPh]}$_n$ having approximately 0.7 toluene solvent molecule per formula unit. Unfortunately it was not possible to obtain X-ray-quality crystals, despite many attempts. Complex **2** was prepared similarly by lithiating a solution of *N*,*N*′-diphenylbenzamidine in toluene, but now in the presence of 1 molar equivalent of hmpa. Orange crystals were isolated after 12 h at room temperature and identified as {Li[PhNC(Ph)NPh]·hmpa}$_2$. Similar lithiations of *N*,*N*′-diphenylbenzamidine in toluene in the presence of tmen or pmdien gave, after refrigeration of the resulting solutions, orange and pale yellow crystals of Li[PhNC(Ph)-NPh]·tmen **3** and Li[PhNC(Ph)NPh]·pmdien **4**, respectively. Complex **5**, {Li[PhNC(Me)NPh]·hmpa}$_2$, the only derivative of *N*,*N*′-diphenylacetamidine reported here, was obtained as cream crystals from the lithiation of this amidine in toluene containing hmpa.

Products **1**–**5** were characterised by analysis and spectroscopic techniques (see Experimental). In addition, **2**–**5** were structurally resolved by single-crystal X-ray diffraction methods. Key bond parameters are listed in Tables 1–4.

The four structurally characterised amidinolithium complexes show both structural similarities and differences. Complexes **3** and **4**, containing the di- and tri-dentate ligands tmen and pmdien respectively, are monomeric. In contrast, use of the unidentate Lewis base hmpa results in dimers **2** and **5**. However, the way in which dimerisation is achieved differs. In **2** a N of a given monomer unit interacts with the Li of the other monomer unit, so forming a $(NLi)_2$ central ring. The hmpa ligands bond terminally to the metal cations. In dimer **5**, however, association is effected by bridging hmpa molecules, resulting in a central $(OLi)_2$ ring. The common structural motif found in all four complexes is that of a planar NCNLi ring. In all cases, the amidinide anion [PhNC(R)NPh]$^-$ uses both N atoms to bond to Li$^+$. However, as discussed below, considerable variation can be found in the N–Li distances and in the central N–C distances within the anion, features explicable in terms of the degree of delocalisation within the NCN unit.

Use of a monodentate hmpa ligand is accompanied by a dimerisation of the core NCNLi unit into the distinctive 'step-like' structure observed for complex **2** (Fig. 1), a system directly analogous to {Li[MeC$_6$H$_4$C(NSiMe$_3$)$_2$]·thf}$_2$.[4a] The dimer has crystallographic inversion symmetry. Within each monomer unit each N of the anion is attached to Li [N(1)–Li(1) 2.046(7), N(2)–Li(1) 2.173(7) Å]. Dimerisation is then achieved by one of these N atoms interacting with Li in the neighbouring monomer unit [N(2)–Li(1A) 2.054(7) Å]. The amidinide anion in **2** possesses distinct asymmetry, with N(1)–C(1) [1.315(4) Å] showing more double- and N(2)–C(1) [1.349(5) Å] more single-bond character. The asymmetry can be explained by examining how charge localisation alters relative bond lengths within the amidinide anion's covalent framework; this effect is greater for **2** than that seen in the analogous stepped dimeric amidinolithium structure {Li[MeC$_6$H$_4$C(NSiMe$_3$)$_2$]·thf}$_2$.[4a] *Ab initio* calculations on model alkali-metal acetaldehyde enolate monomers of form CH_2=CHO^-M^+ have shown how the metal cation localises the charge on the oxygen in the enolate anion.[6] This

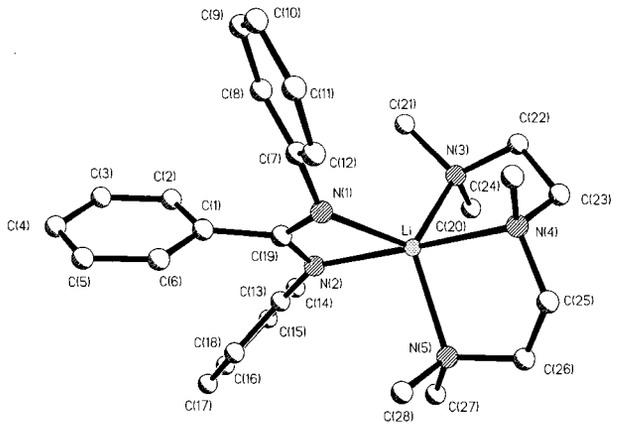


Fig. 3 Molecular structure of Li[PhNC(Ph)NPh]·pmdien **4**

Table 3 Selected bond lengths (Å) and angles (°) for complex **4**

Li–N(1)	2.076(6)	Li–N(2)	2.188(6)
Li–N(3)	2.162(6)	Li–N(4)	2.235(6)
Li–N(5)	2.139(6)	N(1)–C(19)	1.335(4)
N(2)–C(19)	1.336(4)	N(3)–C(22)	1.474(6)
C(22)–C(23)	1.485(7)	N(4)–C(23)	1.444(6)
N(4)–C(25)	1.489(6)	C(25)–C(26)	1.476(6)
N(5)–C(26)	1.446(5)		
N(1)–Li–N(2)	64.4(2)	N(1)–Li–N(3)	116.7(3)
N(1)–Li–N(4)	111.5(3)	N(1)–Li–N(5)	119.2(3)
N(3)–Li–N(2)	64.4(2)	N(2)–Li–N(4)	175.7(3)
N(5)–Li–N(4)	81.9(2)	N(5)–Li–N(2)	98.9(2)
N(3)–Li–N(4)	82.9(2)	N(5)–Li–N(3)	123.9(3)
N(1)–C(19)–N(2)	116.7(3)	C(19)–N(1)–Li	91.8(2)
C(19)–N(2)–Li	87.0(2)	Li–N(3)–C(22)	105.7(3)
C(23)–N(4)–Li	102.9(3)	C(25)–N(4)–Li	105.3(3)
C(26)–N(5)–Li	108.6(3)		

leads to only a modest increase in the C–C length in the anion compared to that in the original alcohol. The vinyl alcohol anion is isoelectronic with the amidinide anion where a similar charge localisation is observed. In **2** nitrogen N(2) interacts with two lithium cations whereas N(1) only interacts with one, hence N(2) sees a significant charge localisation on it relative to N(1). Thus, in a manner analogous to the alkali-metal enolate systems,[6] the almost uniform π delocalisation observed for **3** and **4** (see later) is replaced in **2** by two distinct N–C distances.

The disparity among the C–N bond lengths [1.343(6), 1.323(6), 1.320(7) and 1.331(7) Å] within the silylated NCN moiety of $\{Li[MeC_6H_4C(NSiMe_3)_2]\cdot thf\}_2$ is significantly less than that found in complex **2**. This may be attributed to the presence of silicon feeding electron density into the NCN moiety and thus offsetting the charge-localisation effect of the co-ordinated lithium cations. The Li–N distances in the silylated complex are all different [2.051(10), 2.387(9), 1.993(9), 2.099(9), 2.145(8) and 2.073(8) Å] (attributable to the presence of thf as a donor and the different steric environment presented by the silylated ligand) and do not show the symmetry across the dimer observed for **2**. The 'stepped-dimer' shape of **2** is mainly attributable to steric factors causing the two chelate units to adopt the lowest-energy configuration. Such a step-dimer is not unknown; indeed there are three such $(NCNLi)_2$ dimers in the Cambridge Crystallographic Database.[4a,7,8]

Changing the Lewis-base donor from unidentate hmpa to didentate tmen gives complex **3**. The solid-state structure (Fig. 2) shows it to be monomeric with a four-co-ordinate lithium cation chelated by the η^2-amidinide anion and by a neutral tmen ligand. The core unit is a planar NCNLi four-membered ring in which the amidinide NCN backbone now exhibits uniform C–N distances [1.334(2) Å] suggesting that the anionic charge is fully delocalised over the NCN moiety and that **3** is

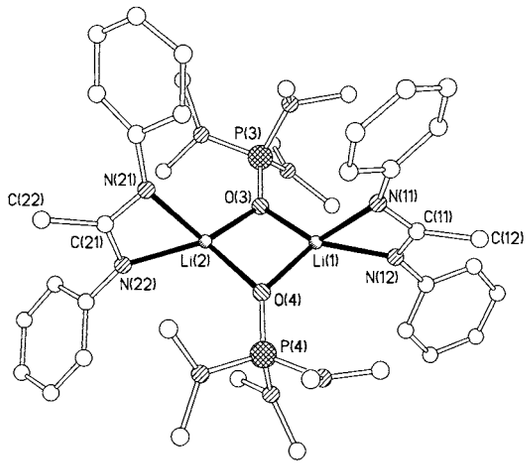


Fig. 4 Molecular structure of $\{Li[PhNC(Me)NPh]\cdot hmpa\}_2$ **5**. Minor disorder components are not shown

Table 4 Selected bond lengths (Å) and angles (°) for complex **5**

Li(1)–O(3)	1.945(12)	Li(1)–O(4)	1.923(13)
Li(1)–N(11)	2.034(13)	Li(1)–N(12)	2.057(12)
Li(2)–O(3)	1.950(14)	Li(2)–O(4)	1.963(13)
Li(2)–N(21)	2.03(2)	Li(2)–N(22)	2.081(14)
N(11)–C(11)	1.323(8)	N(12)–C(11)	1.327(8)
C(11)–C(12)	1.522(9)	N(21)–C(21)	1.330(9)
N(22)–C(21)	1.314(9)	C(21)–C(22)	1.511(10)
O(4)–Li(1)–O(3)	94.1(5)	O(4)–Li(1)–N(11)	117.8(6)
O(3)–Li(1)–N(11)	127.2(7)	O(4)–Li(1)–N(12)	130.4(7)
O(3)–Li(1)–N(12)	123.9(6)	N(11)–Li(1)–N(12)	65.9(4)
O(3)–Li(2)–O(4)	92.7(5)	O(3)–Li(2)–N(21)	117.9(7)
O(4)–Li(2)–N(21)	127.2(7)	O(3)–Li(2)–N(22)	133.2(7)
O(4)–Li(2)–N(22)	123.0(7)	N(21)–Li(2)–N(22)	66.0(5)
C(11)–N(11)–Li(1)	89.8(5)	C(11)–N(12)–Li(1)	88.7(5)
N(11)–C(11)–N(12)	114.3(6)	N(11)–C(11)–C(12)	122.7(7)
N(12)–C(11)–C(12)	122.4(6)	C(21)–N(21)–Li(2)	89.9(6)
C(21)–N(22)–Li(2)	88.2(6)	N(22)–C(21)–N(21)	115.7(7)
N(22)–C(21)–C(22)	120.9(7)	N(21)–C(21)–C(22)	123.1(7)
P(3)–O(3)–Li(1)	134.3(5)	P(3)–O(3)–Li(2)	134.1(5)
Li(1)–O(3)–Li(2)	85.0(5)	P(4)–O(4)–Li(1)	134.6(4)
P(4)–O(4)–Li(2)	136.1(5)	Li(1)–O(4)–Li(2)	85.3(6)

best described as a diazaallyl system. This central NCNLi unit is entirely symmetrical with uniform N–Li distances [2.023(4) Å] complementing the equal C–N distances.

This symmetry is lost on changing the Lewis-base donor from didentate tmen to tridentate pmdien to give complex **4**. As with **3** the solid-state structure (Fig. 3) of **4** is monomeric, but now with a five-co-ordinate lithium cation chelated by the η^2-amidinide anion and by a pmdien donor ligand. The core unit is again a NCNLi four-membered ring which is essentially planar. Within the amidinide unit, **4** exhibits essentially uniform C–N distances [N(2)–C(19) 1.336(4) and N(1)–C(19) 1.335(4) Å] which are almost an exact average of the C=N [1.302(7) Å] and C–N [1.360(8) Å] bond lengths observed in the protonated, uncomplexed amidine,[9] suggesting uniform delocalisation throughout the three-atom central unit. It thus appears that, as with complex **3**, the description of the anion in **4** as a diazaallyl system is highly applicable. This description is supported further by the near planarity of the C(13)–N(2)–C(19)–N(1)–C(7) unit [X–N(2)–C(13) 163.0°, X–N(1)–C(7) 157.2° X = centroid of LiN(1)C(19)N(2) plane] (Fig. 3). The slight deviation from the plane can be explained by the electrostatic repulsion between the nitrogen [N(1),N(2)] sp^2 lone pairs. Such repulsion is largely nullified by the electrostatic attraction of the lithium cation for each nitrogen lone pair pulling the C(13)–N(2)–C(19)–N(1)–C(7) unit towards planarity. Unlike in complex **3** there are two distinct anion–lithium bond lengths [N(2)–Li 2.188(6), N(1)–Li

2.076(6) Å] which are generated by the position of the pmdien ligand; on the N(2) side of the molecule there are two Li–N interactions with the donor pmdien molecule [Li–N(3) and Li–N(5)] compared to only one [Li–N(4)] interaction on the N(1) side. Hence, to gain an even charge distribution around the lithium cation, the Li–N(2) interaction elongates about the average (2.132 Å) and the Li–N(1) interaction shortens.

A small alteration in the amidine ligand used, from *N*,*N*′-diphenyl-benzamidine to -acetamidine, and then lithiation and complexation with hmpa leads to the formation of the bridged dimer complex **5** (Fig. 4). The dimer is composed of two essentially planar NCNLi rings joined by a Li_2O_2 ring formed from bridging μ-hmpa ligands (*cf.* the terminal hmpa ligands found in **2**). The dimer is not symmetric, possessing four distinct Li–N [mean 2.151(13) Å] and Li–O interactions [mean 1.945(13) Å].

In each NCN moiety the C–N bonds are effectively equal, confirming total delocalisation such that each unit is best described as a diazaallyl system. The mean of these four distances (1.324 Å) is almost an exact average of the C=N [1.364(3) Å] and C–N [1.281(3) Å] bond lengths found in protonated acetamidine.[10] A hmpa-bridged dimer structure, as observed for **5**, is a relatively common feature of lithiated organics, there being seven such examples in the Cambridge Crystallographic Database with the first, $[Ph(2\text{-}C_5H_4N)NLi{\cdot}hmpa]_2$, being published in 1984.[7] The P–O bond of hmpa is highly dipolar (ylidic) in nature and better described as $P^+–O^-$ rather than as P=O. As such it is a very strong Lewis base and readily forms strong electrostatic interactions with one, two, or even three lithium cations.

For all four structurally characterised complexes discussed here the NCN angle found in the amidino anion suffers a reduction of about 5° from the angles of 121.5(5) and 121.7(3)° observed for the two parent amidines.[9,10] This is in contrast to the previously reported *N*-silylated amidinolithium complex,[4a] in which the NCN angle hardly alters on co-ordination to the lithium [120.1(4) and 121.2(4)°], no doubt attributable to the influence of the silyl groups. Presumably the energetic stability of the NCNLi chelate moiety compensates for the increased strain in the NCN angle of the amidinolithiums reported here compared to that in the parent amidine.

Comparing complexes **2**–**5** it is clear that a change in either the amidinate ligand or the Lewis base effects a significant change in the solid-state structure observed. Complex **3**, a monomer, contains a symmetrical NCNLi core moiety with the four-co-ordinate lithium cation symmetrically complexed by a tmen ligand. The symmetry about the lithium cation is lost on changing to the tridentate pmdien donor ligand in the similarly monomeric complex **4**. The electrostatic nature of the bonding allows the ligands to find their most energetically stable conformation which is not necessarily symmetrical. Changing from one tridentate pmdien to one unidentate hmpa ligand would give a three-co-ordinate lithium monomer, hence dimerisation occurs to the stepped system observed for **2** which possesses four-co-ordinate, and therefore more charge-satisfied, lithium cations. The structural change from **4** to **2** is accompanied by a corresponding change in the extent of electron delocalisation within the NCN moiety, rationalised earlier by charge-localisation effects occurring in **2**. Maintaining the donor as hmpa, but changing the benzamidine ligand for acetamidine still gives a dimer, **5**, but one in which the hmpa ligands are bridging rather than terminal. The fact that only a seemingly minor change in the parent amidine causes such a marked structural change in the complex suggests that the two dimeric types are relatively close in energy. This conclusion is backed up by the characterisation of two such structural isomers of $[Ph(2\text{-}C_5H_4N)NLi{\cdot}hmpa]_2$ in one and the same crystal structure; a stepped dimer with terminal hmpa ligands and a hmpa-bridged dimer.[7]

The four structures discussed in this paper show how a change in the denticity of the Lewis-base donor ligands utilised and/or a small alteration of the amidine ligand can have a significant effect on the solid-state structure of the system.

Experimental

Preparations

Compound 1. To a solution of *N*,*N*′-diphenylbenzamidine (2.5 mmol, 0.68 g) in dry toluene (6 cm^3) (chilled in a liquid-N_2 bath) was added 1.6 mol dm^{-3} *n*-butyllithium (2.5 mmol, 1.6 cm^3) in hexane. The solution was allowed to warm to room temperature with constant stirring, giving a yellow solution and precipitate. Strong heating gave a clear yellow-brown solution. Cooling to room temperature yielded a crop of yellow, air-sensitive microcrystals of compound **1** after 12 h (0.085 g, 12%), m.p. > 320 °C (Found: C, 80.9; H, 5.9; N, 8.4. $C_{19}H_{15}LiN_2{\cdot}0.7C_7H_8$ requires C, 83.8; H, 6.0; N, 8.1%). ^{1}H NMR (250 MHz in [$^2H_8$]thf, 293 K): δ 7.45 (m, 2 H, aryl), 7.30–7.10 (m, 6.4 H, aryl), 6.85 (m, 8.3 H, aryl), 6.40 (tt, 2 H, aryl) and 2.3 (s, 2.2 H, C_6H_5*Me*)].

Complex 2. To a solution of *N*,*N*′-diphenylbenzamidine (2.5 mmol, 0.68 g) and hmpa (2.5 mmol, 0.45 cm^3) in dry toluene (6 cm^3) (chilled in a liquid-N_2 bath) was added 1.6 mol dm^{-3} $LiBu^n$ (2.5 mmol, 1.6 cm^3) in hexane. The solution was allowed to warm to room temperature with constant stirring, giving an orange solution and precipitate. Strong heating gave a clear orange solution which was left to cool to room temperature. After 12 h orange, air-sensitive crystals of complex **2** were isolated (0.64 g, 56%), m.p. 212–215 °C (Found: C, 64.3; H, 7.0; N, 15.4. $C_{25}H_{33}LiN_5OP$ requires C, 65.7; H, 7.2; N, 15.3%). ^{1}H NMR: δ 7.34–6.73 (series of broad poorly resolved d and t, 15 H, *Ph*NC*Ph*N*Ph*) and 2.38 (d, 18 H, hmpa).

Complex 3. To a solution of *N*,*N*′-diphenylbenzamidine (20 mmol, 5.45 g) in dry toluene (50 cm^3) (chilled in an ice-bath) was added 1.6 mol dm^{-3} $LiBu^n$ (20 mmol, 12.8 cm^3) in hexane. The resulting yellow-green solution was allowed to warm to room temperature with constant stirring over 2 h, after which time tmen (20 mmol, 3 cm^3) was added. Gentle heating gave a clear solution which was filtered and reduced to one third volume *in vacuo*. Refrigeration at −20 °C for 2 d yielded bright orange, air-sensitive crystals of complex **3** (6 g, 77%), m.p. 128–131 °C (Found: C, 74.8; H, 7.6; N, 13.9. $C_{25}H_{31}LiN_4$ requires C, 76.1; H, 7.9; N, 14.2%). ^{1}H NMR (200 MHz, [$^2H_8$]thf, 303 K): δ 8.3–6.7 (4 broad unresolved s, 15 H, *Ph*NC*Ph*N*Ph*), 2.41 (s, 4 H, $Me_2NCH_2CH_2NMe_2$) and 2.25 (s, 12 H, $Me_2NCH_2CH_2NMe_2$).

Complex 4. To a solution of *N*,*N*′-diphenylbenzamidine (5 mmol, 1.36 g) and pmdien (5 mmol, 1.05 cm^3) in toluene (4 cm^3)–thf (3 cm^3) (chilled in a liquid-N_2 bath) was added 1.6 mol dm^{-3} $LiBu^n$ (5 mmol, 3.2 cm^3) in hexane. The solution was allowed to warm to room temperature with constant stirring. Gentle heating gave a clear dark orange solution from which half the solvent was removed *in vacuo*, followed by layering with hexane (2 cm^3). Refrigeration at −20 °C for 2 d yielded pale yellow, air-sensitive crystals of complex **4** (1.25 g, 55%), m.p. 151–153 °C (Found: C, 73.5; H, 8.3; N, 14.9. $C_{28}H_{38}LiN_5$ requires C, 74.5; H, 8.4; N, 15.5%). ^{1}H NMR (250 MHz, [$^2H_8$]thf, 293 K): δ 8.5–6.5 (series of broad unresolved s, 15 H, *Ph*NC*Ph*N*Ph*), 2.5–2.3 (m, 8 H), 2.33 (s, 3 H) and 2.16 (s, 12 H) (all pmdien, 23 H).

Complex 5. To a solution of *N*,*N*′-diphenylacetamidine (2.5 mmol, 0.53 g) and hmpa (2.5 mmol, 0.45 cm^3) in dry toluene (6 cm^3) (chilled in a liquid-N_2 bath) was added 1.6 mol dm^{-3} $LiBu^n$ (2.5 mmol, 1.6 cm^3) in hexane. The solution was allowed to warm to room temperature with constant stirring giving a pale yellow solution and precipitate. Gentle heating gave a clear yellow solution which was left to cool to room temperature. After 12 h cream, air-sensitive crystals of complex **5** were isolated (0.91 g, 92%), m.p. 134–137 °C (Found: C, 59.4; H, 8.3; N, 17.8.

Table 5 Summary of crystal structure data for complexes **2**–**5**

	2	**3**	**4**	**5**
Formula	$C_{50}H_{66}Li_2N_{10}O_2P_2$	$C_{25}H_{31}LiN_4$	$C_{28}H_{38}LiN_5$	$C_{40}H_{62}Li_2N_{10}O_2P_2$
M	914.9	394.48	451.57	790.8
Crystal dimensions/mm	0.27 × 0.30 × 0.33	0.8 × 0.3 × 0.3	0.25 × 0.25 × 0.25	0.35 × 0.35 × 0.32
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*1 (no. 2)	*C*2/*c* (no. 15)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)
a/Å	9.924(2)	12.030(4)	11.873(2)	11.610(2)
b/Å	11.649(2)	16.021(5)	18.103(4)	11.428(2)
c/Å	12.196(2)	12.232(6)	12.774(3)	34.893(7)
α/°	97.72(3)	—	—	—
β/°	100.45(3)	93.83(4)	90.08(3)	98.47(3)
γ/°	107.87(3)	—	—	—
U/Å^3	1292.2(4)	2352(2)	2745.6(10)	4579(2)
Z	1	4	4	4
D_c/g cm^{-3}	1.176	1.114	1.092	1.147
F(000)	488	848	976	1696
μ/mm^{-1}	0.132	0.066	0.065	1.201
T/K	153(2)	293(2)	153(2)	250(2)
θ Range/°	3.59–22.49	2.54–27.48	2.60–22.50	2.5–55.0
Maximum *h*, *k*, *l* indices	10, 12, 13	14, 20, 15	12, 19, 13	12, 12, 37
No. reflections collected	3925	3950	6059	5746
No. independent reflections	3373	2231	3579	5746
R_{int}	0.052	0.0430	0.019	0
No. refined parameters	304	200	312	610
Weighting parameters *a*, *b*	0.1055, 0.00	0.0542, 0.0692	0.1802, 1.0740	0.0616, 8.4971
Extinction coefficient	—	—	—	0.000 36 (11)
R^a (observed reflections)	0.0537 (2521)	0.0420 (1223)	0.0649 (2920)	0.0630 (3062)
R'^b (all data)	0.1828	0.1158	0.2628	0.2322
Goodness of fit on F^2	1.204	1.032	1.173	1.061
Largest difference map features/e Å^{-3}	+0.54, −0.65	+0.20, −0.23	+0.56, −0.80	+0.57, −0.30

Parameters in common: Mo-Kα radiation, λ = 0.710 73 Å; Cu-Kα for complex **5**, λ = 1.541 84 Å. ^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for reflections with $F_o^2 > 2\sigma(F_o^2)$. ^{b} $R' = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(F_o^2)^2]^{\frac{1}{2}}$.

$C_{20}H_{31}LiN_5OP$ requires C, 60.8; H, 7.9; N, 17.7%). ^{1}H NMR [250 MHz, $(CD_3)_2SO$, 293 K]: δ 6.94 (m, 8 H, *Ph*NCMeN*Ph*), 6.56 (nonet, 2 H, *Ph*NCMeN*Ph*), 2.52 (d, 18 H, hmpa) and 1.80 (s, 3 H, PhNC*Me*NPh).

Crystallography

Crystals of complexes **2**, **4** and **5** were examined on Stoe-Siemens diffractometers equipped with Oxford Cryostream crystal-cooling devices.[11] Cell parameters were refined from 2θ values of selected strong reflections measured at ±ω to minimise systematic errors. Intensities were measured with ω–θ scans and on-line profile fitting.[12] Crystals of **3** were examined on a Rigaku AFC6S diffractometer. Intensities were measured with ω–2θ scans and with fixed backgrounds. Crystal data and other information on the structure determination procedures are given in Table 5.

The structures were solved by direct methods[13] and refinement, based on F^2, was by full-matrix least-squares techniques,[14] with weighting $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + (bP)]$, where $P = (F_o^2 + 2F_c^2)/3$. The isotropic extinction coefficient x is defined such that F_c is multiplied by $(1 + 0.001xF_c^2\lambda^3/\sin 2\theta)^{-\frac{1}{4}}$. Non-hydrogen atoms were refined with anisotropic displacement parameters, and isotropic H atoms were constrained with a riding model.

Extensive disorder was found only in the structure of complex **5**. Two alternative positions were resolved and refined for atoms in three parts of the structure: one phenyl substituent, with occupancy factors 0.63:0.37(4); one methyl group of one hmpa, 0.55:0.45(2); most atoms of the other hmpa, 0.557:0.443(10). Restraints were applied to geometry and displacement parameters in the disordered groups.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc.*, *Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/374.

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